

COMPOSITION AND PROCESS FOR ETCHING AND DESMUTTING
ALUMINUM AND ITS ALLOYS

CROSS-REFERENCE TO RELATED APPLICATIONS

5 This application claims the benefit of U.S. provisional application
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BACKGROUND OF THE INVENTION

1. Field of the Invention

10 This invention relates to compositions and processes that enable
surfaces of aluminum and its alloys to be etched without requiring a subsequent
“desmutting” step. The invention is particularly useful with copper and zinc
containing aluminum alloys that are typically used in forming parts suitable for the
aerospace industry, such as airplane components.

2. Background Art

15 Chemical and mechanical treatments of aluminum and its alloys often
leave the surface with a dark coating that must be removed before subsequent
surface finishing steps can be satisfactorily completed. This process is generally
known in the art as “desmutting” or sometimes as “deoxidizing.” The dark coating
requiring desmutting comprises residual intermetallic aluminum alloying agents;
20 such as copper, zinc, silicon and iron, that remain on the surface of etched
aluminum or aluminum alloy. The conventional desmutting compositions have
normally included concentrated nitric and/or sulfuric acid and chromates, with
fluorides, ferric ions, oxidizers such as persulfate and peroxide, and ferricyanide
all serving as frequently used optional ingredients. In recent years there has been
25 environmentally driven incentive to avoid the use of chromates and ferricyanides,
but no fully satisfactory deoxidizer free from these materials is believed to have
been developed. Accordingly, it would be desirable to provide a composition and

process that could etch aluminum and its alloys without requiring a subsequent desmutting step.

SUMMARY OF THE INVENTION

It has been found that certain acidic etchant compositions containing
5 sulfuric acid, nitric acid, phosphoric acid, and a stabilized oxidant will essentially
simultaneously etch and desmut surfaces of aluminum and its alloys. Notably,
triethanolamine and sodium sulfide, components that are typically present in prior
art alkaline etchant compositions, are not present in the acidic etchant of the present
invention. Also, the acidic etchant composition of the present invention eliminates
10 the need for a subsequent desmutting step and thus the use of chromium, iron, and
fluorine components that are typically found in desmutting compositions. Thus, the
etching and desmutting of aluminum alloys may be done in one processing step in
lieu of the two-step alkaline etching and desmutting process.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Embodiments of the present invention comprise a method and an
15 acidic aqueous composition for etching and simultaneously desmutting of aluminum
and its alloys, wherein the aqueous composition comprises, preferably consists
essentially of, and more preferably consists of, water and:

- (A) an acid source comprising sulfuric acid and nitric acid;
- 20 (B) a non-fluorine containing etchant source comprising
phosphoric acid; and
- (C) a stabilized oxidant; and optionally one or more of the
following:
- (D) a wetting agent and/or a degassing agent; and
- 25 (E) a complexing agent and/or a grain modifier.

In a preferred embodiment, the composition comprises water and:

- (1) diluted sulphuric acid;
- (2) nitric acid;

- (3) phosphoric acid;
- (4) molybdate and/or condensed molybdate ions;
- (5) a perfluoroalkyl sulfonate; and
- (6) aluminum sulfate.

5 Various embodiments of the invention include working compositions
for direct use in treating metals, concentrates and partial concentrates from which
such working compositions can be prepared by dilution with water and/or mixing
with other chemically distinct concentrates, processes for treating metals with a
composition according to the invention, and extended processes including additional
10 steps that are conventional per se, such as rinsing, and, particularly advantageously,
subsequent conversion coating, anodizing, fusion welding, penetrant dyeing and/or
painting or some similar overcoating process that puts into place an organic binder
containing protective coating over the metal surface treated according to a narrower
embodiment of the invention. Articles of manufacture including surfaces treated
15 according to a process of the invention are also within the scope of the invention.

For a variety of reasons, it is preferred that compositions according
to the invention, as defined above, should be substantially free from many
ingredients used in compositions for similar purposes in the prior art. Specifically,
it is increasingly preferred in the order given, independently for each preferably
20 minimized component listed below, that these compositions, when directly contacted
with metal in a process according to this invention, contain no more than 1.0, 0.35,
0.10, 0.08, 0.04, 0.02, 0.01, 0.001, or 0.0002, percent of each of the following
constituents: hexavalent chromium; iron compounds; silica; silicates that do not
contain at least four atoms of fluorine per atom of silicon (fluoroalkyl silicon
25 compounds); ferricyanide; ferrocyanide; thiourea; sugars; glycerine; α -
glucoheptanoic acid and its salts; and salts thereof.

The components in the preferred composition are preferably, more
preferably, and most preferably present in the following weight percents, based on
total weight of the compositions:

Component	Preferred Range (wt. %)	More Preferred Range (wt. %)	Most Preferred Range (wt. %)
1	10 - 50	12 - 35	18 - 25
2	0.5 - 15	1 - 10	2.5 - 7.5
3	25 - 90	35 - 85	45 - 70
4	0.01 - 2	0.01 - 0.75	.05 - .25
5	0 - 0.1	0.0001 - 0.01	.0005 - .005
6	0 - 10	0.5 - 5	1 - 3
Water	5 - 50	10 - 35	16 - 20

10 The acid source (A) comprises acids that are capable of holding ions of aluminum intermetallic alloying elements (copper, zinc, silicon, and iron) in solution. The acid source (A) preferably comprises sulfuric acid (1) and nitric acid (2).

15 Preferably, but not necessarily, the sulfuric acid (1) comprises diluted sulfuric acid. By diluted sulfuric acid, it is meant an aqueous solution of sulfuric acid containing less than 80 wt.% (water comprising the other 20%), most preferably 55 wt.% sulfuric acid, based on the total weight of the aqueous sulfuric acid solution. Most preferably, the sulfuric acid (1) comprises Base 443, a pre-reacted/diluted roughly 45% by weight sulfuric acid solution used by Henkel that
20 comprises a 50% solution of Sulfuric Acid 66° Baume, a 93% sulfuric acid solution available from Ashland Chemical Company of Boonton, NJ.

25 Preferably, but not necessarily, the nitric acid (2) comprises concentrated nitric acid. By concentrated nitric acid, it is meant an aqueous solution of nitric acid containing 45 to 75 wt.% nitric acid, more preferably 64 to 70 wt.% nitric acid, and most preferably 66 to 68 wt.% nitric acid, based on the total weight of the aqueous nitric acid solution. A preferred nitric acid (2) comprises nitric acid 42°, a commercial grade nitric acid (a 67% by weight solution) having a specific gravity of 42° Baume available from Dupont of Wilmington, DE.

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The etchant source (B) comprises a compound that primarily
functions to remove ionized aluminum metal at a given rate in lieu of fluorine. The
etchant source (B) preferably comprises phosphoric acid (3). Preferably, but not
necessarily, the phosphoric acid (3) comprises diluted phosphoric acid. By diluted
5 phosphoric acid, it is meant an aqueous solution of phosphoric acid containing less
than 95 wt. %, and most preferably 75 wt. % phosphoric acid. The most preferred
etchant source (B) comprises Phosphoric Acid 75%, by weight, aqueous solution
of phosphoric acid available from Quadra Corporation of Huntersville, NC.

The stabilized oxidant (C) comprises one or more compounds that
10 primarily function to oxidize and ionize ground state metals, such as copper, zinc,
silicon, and iron, that are present in aluminum alloys to the divalent transition state
to create in-situ acid metal salts that are then able to be solubilized by the etchant
source (B). The stabilized oxidant (C) helps to minimize the generation of NO_x .
The stabilized oxidant (C) can be either inorganic or organic, and preferably
15 comprises molybdate and/or condensed molybdate ions (4). Because the degree of
aggregation of molybdate ions is usually uncertain and is not believed to affect the
favorable action of molybdate ions in compositions according to this invention, the
concentration of these ions is described herein as the stoichiometric equivalent as
molybdenum atoms, even though only those molybdenum atoms that are present in
20 some form of molybdate or condensed molybdate anions are believed to be
effective. A preferred stabilized oxidant (C) comprises Ammonium Molybdate
available from Climax Molybdenum Company (Division of Cyprus Climax Metals)
of Tempe, AZ.

For component (D), almost any surfactant or wetting agent that is
25 effective to lower the surface tension and solubilize any organic contaminants
present on the surface to be treated could be used in principle.

Surfactants which have been found to be satisfactorily stable,
adequate in reducing surface tensions of the compositions while not making them
intolerably prone to foaming, and effective in keeping dried areas from forming
30 during transfer times up to at least 3 minutes between treatment and rinsing, and

which are therefore particularly preferred, are alkyl carboxyl derivatives and perfluoroalkyl sulfonates with amphoteric mixes.

Component (D) can also comprise any suitable degassing agent known in the art that is capable of changing the size and/or structures of the foaming bubbles which operates to retard and/or prevent the formation of noxious gases such as NO_x , SO_x , to name a few.

Component (D) may comprise one compound that operates both as a wetting agent and a degassing agent, or one or more compounds that operate independently as a wetting agent or a degassing agent.

A particularly preferred Component (D) comprises the oxidant stable surfactant Zonyl FSN-100, a perfluoroalkyl sulfonate (5), available from DuPont. Zonyl FSN-100 operates both as a wetting agent and a degassing agent.

Component (E) may comprise any suitable complexing agent/grain modifier that is known in the art. A particularly preferred Component (E) comprises aluminum sulfate (6) available from General Alum and Chemical Corporation of Holland, OH, under the name Aluminum Sulfate, LQ.

One preferred method of making a preferred composition of the present invention comprises adding water to a mixing tank, and preferably a stainless steel or acid-resistant plastic mixing tank, and turning on the agitator. Then the pre-diluted sulfuric acid (1) is added to the tank. Next, the molybdate (4) is sifted in and mixed until dissolved. The remaining ingredients (2), (3), (5) and (6) are then mixed in until a uniform composition results.

A working composition according to the invention may be applied to a metal surface to be treated by any convenient method, several of which will be readily apparent to those skilled in the art. Immersion is the simplest and is

believed most often used. However, spraying, roll coating, and the like can also be used.

5 The temperature during contact and time of contact between the composition according to the invention and the metal to be treated thereby may be varied within wide limits to achieve the desired effects, which can often be determined by visual inspection of the metal surface, after rinsing if necessary. As a general guideline, the temperature normally preferably is, with increasing preference in the order given, not less than 20°C or 30°C and independently preferably is, with increasing preference in the order given, not more than 80°C or 10 60°C, and the time of contact normally preferably is, with increasing preference in the order given, not less than 0.1, 0.5, 1.0, 1.5, 1.8, or 2.0 minutes and independently preferably is, with increasing preference in the order given, not more than 180, 120, 60, or 30 minutes.

15 After treatment according to this invention, the treated surfaces are normally rinsed with water before any subsequent treatment. Preferably, the rinsing is completed as soon as practical after removing the treated surfaces from contact with the etchant composition, and if at all practicable should at least be completed before the etchant composition has dried into place on any part of the surface. After rinsing the surfaces often are also dried. Rinsing, drying, and any subsequent 20 treatments are generally performed using suitable manners known in the art.

Preferably, the invention is used in connection with wrought aluminum alloys containing copper and zinc. The invention is particularly advantageously adapted to the treatment of aluminum alloys 7150, 7075, 2024, 2324, and 6061.

25 During extended use of the etchant composition according to this invention, new constituents may be introduced into the etchant composition by dissolution of the metal objects treated, and some of the constituents of the bath may be consumed by reaction. Therefore, as with other similar treatments, if very long term operation is desired, it is advantageous to withdraw a portion of the

composition continuously for removal of any unwanted constituents and to replenish depleted desirable constituents. In some cases, only replenishment may be satisfactory, or no treatment of the composition at all may be required.

5 The practice of this invention may be further appreciated by consideration of the following, non-limiting, working example.

Example:

	Parts/Weight (lbs)	Component
	172.4900	WATER TAP
	200.0000	BASE 443
	1.5000	AMMONIUM MOLYBDATE
	560.0000	PHOSPHORIC ACID 75%
	50.0000	NITRIC ACID 42°
	16.0000	ALUMINUM SULFATE, LQ, TECH GRD
	.0100	ZONYL FSN-100
Totals:	1000.0000 lbs.	

10 The above working composition was prepared by adding the water to a mixing tank, preferably a stainless steel or acid-resistant plastic tank, and turning on the agitator, following which Base 443 is added to the tank. The ammonium molybdate is then sifted in and the mixture agitated until the ammonium molybdate is dissolved. Next, the phosphoric acid, nitric acid, aluminum sulfate and Zonyl FSN-100 (which has been heated to between 100° - 120°F to liquify) are
15 added and agitated for 30 minutes or until the Zonyl FSN-100 has dissolved.

Parts made of the aluminum alloys 2024-T3 and 7075-T6 were then exposed to the above working composition for 15 minutes. The parts were observed to be etched and +desmuted.

Except where otherwise expressly indicated, all numerical quantities indicating amounts of material or conditions of reaction and/or use herein are to be understood as modified by the word "about" in describing the broadest scope of the invention. Practice within the numerical limits stated is generally preferred. Also,
5 unless expressly stated to the contrary: percent, "parts of", and ratio values are by weight based on total weight of the composition of solutions; the description of a group or class of materials as suitable or preferred for a given purpose in connection with the invention implies that mixtures of any two or more of the members of the group or class are equally suitable or preferred; description of
10 constituents in chemical terms refers to the constituents at the time of addition to any combination specified in the description, and does not necessarily preclude chemical interactions among the constituents of a mixture once mixed; specification of materials in ionic form implies the presence of sufficient counterions to produce electrical neutrality for the composition as a whole, and any counterions thus
15 implicitly specified should preferably be selected from among other constituents explicitly specified in ionic form, to the extent possible; otherwise such counterions may be freely selected, except for avoiding counterions that act adversely to the objects of the invention; the term "mole" means "gram mole", and "mole" and its variations may be applied herein to ionic or any other chemical species with defined
20 numbers and types of atoms, as well as to chemical substances with well defined conventional molecules.

While embodiments of this invention have been illustrated and described, it is not intended that these embodiments illustrate or describe all possible forms of the invention. Rather, the words used in the specification are
25 words of description rather than limitation, and it is understood that various changes may be made without departing from the spirit and scope of the invention.